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Indian Standard

METHODS FOR DETERMINATION OF ARSENIC

(Second Revision)

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Indian Standard

METHODS FOR DETERMINATION OF ARSENIC

(Second Revision)

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 15 June 1983, after the draft finalized by the Chemical Standards Sectional Committee had been approved by the Chemical Division Council.

0.2 This standard was first published in 1962 covering only modified Gutzeit method. Newer techniques for determination of arsenic had been increasingly applied, and one such method was based on silver diethyldithiocarbamate. The standard was revised in 1971 to incorporate this method. This method assists in determining the actual arsenic content as against the limit test provided by modified Gutzeit method. Selection of either silver diethyldithiocarbamate or modified Gutzeit method has to be judged from the end use.

0.3 The second revision of the standard has been undertaken to align it with ISO 2590-1973 'General method for the determination of arsenic — Silver diethyldithiocarbamate photometric method', issued by the International Organization for Standardization. Assistance has also been derived from the Doc : 47/1 N. 62 'General method for the diethyldithiocarbamate photometric method', issued by the International Organization for Standardization.

0.4 Before the test can be applied to the material, any arsenic present has to be quantitatively converted into its simple derivatives like arsenic trichloride or pentachloride which can be completely reduced to arsine by action of zinc in presence of dilute acid. These derivatives should be free from interfering substances like nitrate, copper, silver, mercury, cobalt, nickel, molybdenum and palladium which are to be removed suitably and taken in the desired volume containing the desired amount of free acid. Though the preparation of test solution shall be dealt by individual material specifications, the possible treatments either alone or in combination, will be suitable for most samples. Such treatments are prescribed in Appendix A for guidance.

0.5 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

1. SCOPE

1.1 This standard prescribes methods for determination of arsenic.

1.1.1 Modified Gutzeit method of test for arsenic shall be employed in cases where the actual arsenic content is not needed and only a knowledge of limit is desired. In cases where the actual arsenic content is to be determined, silver diethyldithiocarbamate method shall be followed. The method is applicable to quantities of arsenic (as As) in the range of 1 to 20 μg.

2. APPARATUS

2.1 The apparatus for modified Gutzeit method shall be as given in Fig. 1.

2.2 For silver diethyldithiocarbamate method the apparatus shall consist of the following.

2.2.1 *Evolution and Absorption Apparatus* — It shall consist of a conical flask *A* of 100 ml capacity for evolution of arsine, a connecting tube *B* to trap hydrogen sulphide, and absorption tube *C* with a spherical or conical groundglass joint. A spring clip may be used to ensure firm joint between the connecting tube *B* and absorption tube *C* when a spherical joint is used. Suitable forms of apparatus using spherical joint with fritted glass are shown in Fig. 2, 3 and 4.

2.2.2 *Spectrophotometer or Photoelectric Absorptiometer* — With filters in the range 520 to 560 nm and 10 mm cells.

NOTE — The glassware should not be rinsed with organic solvents to facilitate drying. Traces of organic matter, especially, acetone may adversely affect the reaction between zinc and acid.

3. QUALITY OF REAGENTS

3.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1977†) shall be employed.

3.2 All the reagents used shall be free from arsenic.

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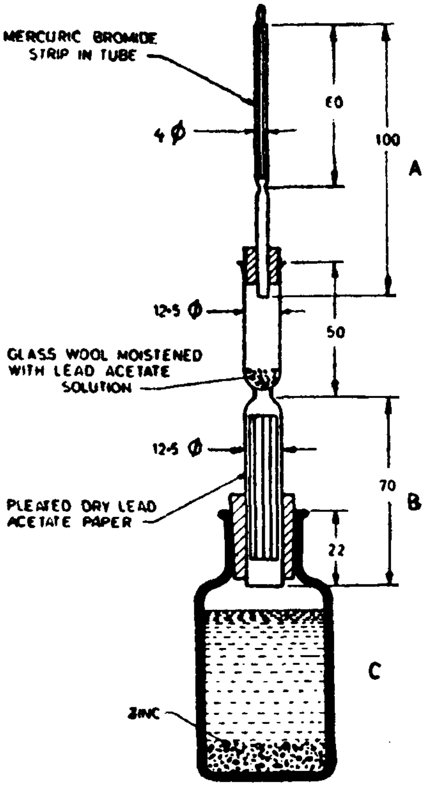
*Rules for rounding off numerical values (*revised*).

†Specification for water for general laboratory use (*second revision*).



All dimensions in millimetres.

FIG. 1 APPARATUS FOR TEST OF ARSENIC (MODIFIED GUTZEIT METHOD)

4. REAGENTS

4.1 Lead Acetate Solution — 10 percent (*m/v*). Add sufficient acetic acid (*see* IS : 695-1975*) to obtain a clear solution.

4.2 Lead Acetate Paper Strips — Soak filter paper strips of 70 × 50 mm size in lead acetate solution contained in a glass bottle. Before use, take out the strips and dry them in an atmosphere free from hydrogen sulphide.

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*Specification for acetic acid ((*second revision*).

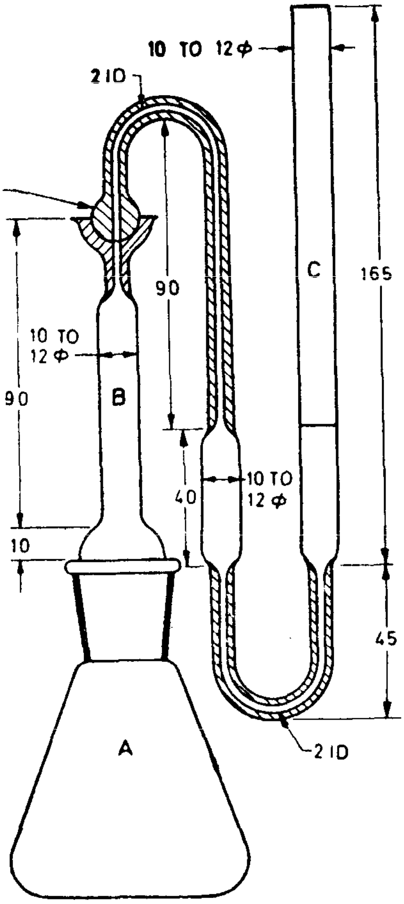

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FIG. 2 APPARATUS FOR ARSENIC DETERMINATION

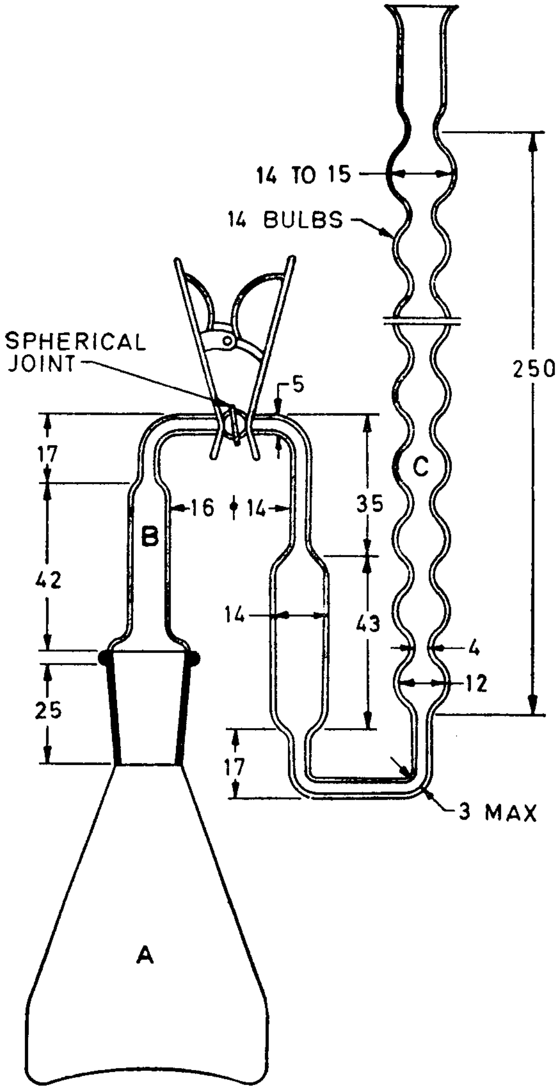

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FIG. 3 APPARATUS FOR DETERMINATION OF ARSENIC (SILVER DIETHYLDITHIOCARBAMATE METHOD)

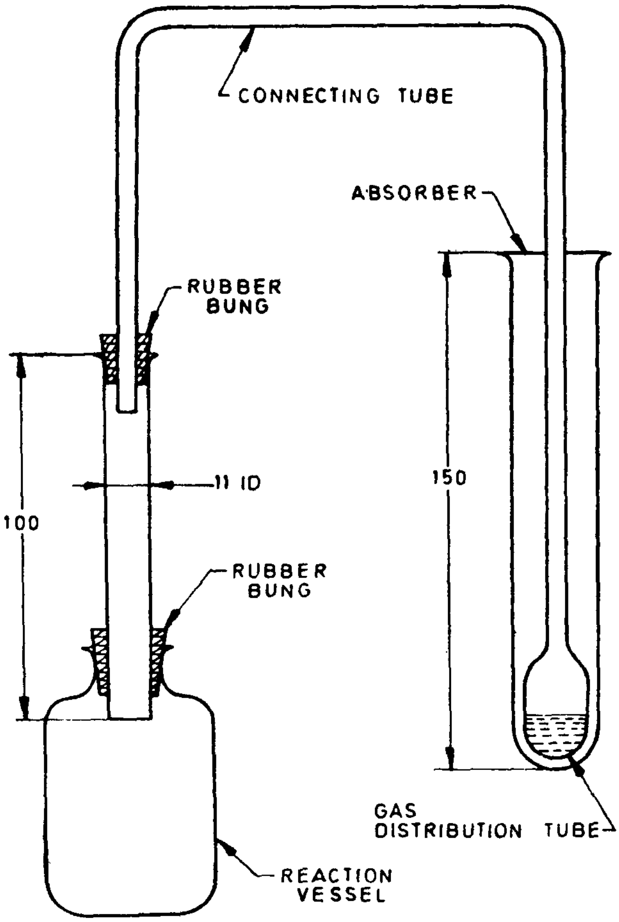

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FIG. 4 APPARATUS WITH FRITTED GLASS FOR DETERMINATION OF ARSENIC (SILVER DIETHYLDITHIOCARBAMATE METHOD)

4.2.1 *Absorbent Cotton Wool Impregnated with Lead Acetate* — Saturate cotton wool with lead acetate solution, drain press and dry under vacuum at room temperature.

4.3 Mercuric Bromide Solution — Dissolve 5 g of mercuric bromide in 100 ml of rectified spirit (*see* IS : 323-1959*).

4.4 Sensitized Mercuric Bromide Paper Strips — Soak filter paper strips cut to a size of 70 × 50 mm in mercuric bromide solution contained in an amber-coloured glass bottle in dark. Before use, remove the strip, press it between sheets of filter paper, and dry it in an atmosphere free from hydrogen sulphide.

4.5 Dilute Sulphuric Acid — approximately 5 N.

4.6 Concentrated Hydrochloric Acid — *see* IS : 265-1976†.

4.7 Potassium Iodide Solution — 15 percent (*m/v*).

4.8 Stannous Chloride Solution — Dissolve 40 g of stannous chloride in 100 ml of hydrochloric acid. Discard this solution if an appreciable deposit forms.

4.9 Zinc — granules, of size 0·5 to 1·0 mm.

4.10 Standard Arsenic Stock Solution — Weigh, to the nearest 0·1 mg, 0·132 0 g of arsenic trioxide and transfer it to a beaker of suitable capacity (for example 100 ml). Dissolve the arsenic trioxide with 2 ml of sodium hydroxide solution containing 50 g/l. Transfer the solution to a 1 000-ml volumetric flask. Wash the beaker several times. Collect the washings in the volumetric flask and make up the volume. One millilitre of this standard solution contains 100 µg of arsenic (As).

4.10.1 *Diluted Standard Arsenic Solution* — containing 2·5 mg of arsenic per litre. Take 25 ml of the standard arsenic solution, transfer it to a 1 000-ml volumetric flask and make up the volume. Prepare this solution at the time of use. One millilitre of this standard solution contains 2·5 µg of arsenic (As).

4.11 Silver Diethyldithiocarbamate Solution — Dissolve 1 g of silver diethyldithiocarbamate in water-white pyridine and dilute to 200 ml with pyridine. Store the solution in stoppered-glass bottles away from light.

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*Specification for rectified spirit (*revised*).

†Specification for hydrochloric acid (*second revision*).

4.11.1 Silver diethyldithiocarbamate may be commercially available or it may be prepared from sodium diethyldithiocarbamate as follows:

> 'Dissolve 10 g of sodium diethyldithiocarbamate [(C_2H_5)$_2$N. CS.SNa_2,$3H_2O$] in 35 ml of rectified spirit (IS : 323-1959*) and filter. Add to the solution with stirring, 100 ml of ether (*see* IS : 336-1973†). Filter it by using suction, wash the precipitate with ether and dry them in air. Dissolve separately 2 2 g of the material in 100 ml of water, and 1·7 g of silver *nitrate in* 100 *ml* of water. Slowly mix these two solutions with constant stirring. Keep the temperature of the mixture below 10°C. Decant the supernatant liquid, wash the precipitate 3 or 4 times with water, at a temperature below 10°C. Filter and dry the product in vacuum at room temperature. Preserve the material protected from light in a cool place. This silver diethyldithiocarbamate solution in water white pyridine is stable for about 2 months.'

NOTE — Alternatively, silver diethyldithiocarbamate may be prepared as follows:

> ' Dissolve 2·2 g of freshly purified sodium diethyldithiocarbamate (as described above) in 250 *ml of* water-white pyridine. Dissolve 1·95 g silver nitrate in 250 ml of water-white pyridine. With continuous stirring pour the former solution into the latter. Allow to stand over-night and filter through a fast filter paper. Store the solution in a well-stoppered dark coloured bottle protected from light in a cool place. The solution is stable for at least 3 months.'

5. PROCEDURE

5.1 Modified Gutzeit Method — Prepare the solution of the material as specified in the individual material specification (*see* also Appendix A). Place the dry lead acetate paper in the lower portion of the tube *B* and cotton wool moistened with lead acetate in its upper portion. Place the sensitized strip of mercuric bromide paper in tube *A* and connect the tubes together with a rubber stopper. Introduce the solution of the material into the bottle *C* and add 10 ml of dilute sulphuric acid. Add 0·5 ml of stannous chloride solution, 5 ml of potassium iodide solution and make up the volume with water to about 50 ml. Mix the contents and drop in about 10 g of zinc. Fit in position the rubber stopper carrying the tube *B* immediately. Place the bottle in a warm place at about 40°C. Remove the test strips after 40 minutes with the help of tweezers. Conduct the test in exactly similar manner by using a volume of standard arsenic solution as specified in the material specification, in place of the solution of the material and compare the stain produced with the material with that produced with the arsenic solution.

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*Specification for rectified spirit (*revised*).

†Specification for ether (*revised*).

5.1.1 The limit prescribed in the material specification shall be taken as not having been exceeded if the length of the stain as well as the intensity of its colour produced in the test with the material is not greater than those produced with the corresponding standard arsenic solution.

5.2 Silver Diethyldithiocarbamate Method

Principle — Absorption of arsine in a solution of silver diethyldithiocarbamate involves the reaction:

$$AsH_3 + 6\ Ag\ (DDTC) = 6\ Ag + 3\ H\ (DDTC) + As\ (DDTC)_3$$

The colloidally dispersed silver, purplish-red colour, is measured by photometry (nephelometry) at 540 nm.

5.2.1 *Preparation of Calibration Curve* — The curve shall be confirmed every time when a new solution of silver diethyldithiocarbamate is prepared.

5.2.2 *Evolution of Arsine* — Transfer to a series of 100 ml conical flasks, aliquots of standard arsenic solution corresponding to 0, 5, 10, 15, 20 and 25 µg of arsenic and proceed as given in **5.2.2.1**.

5.2.2.1 Add 10 ml of concentrated hydrochloric acid and dilute to 50 ± 5 ml with water. Add 2 ml of potassium iodide and stannous chloride solution respectively. Mix well and let it stand for 15 to 20 minutes. Pack lightly the top third of the connecting tube with impregnated absorbent cotton wool and assemble an the absorption train. Transfer 5·0 ml of silver diethyldithiocarbamate solution to absorption tube *C*. After 15 to 20 minutes, introduce 5 g of zinc granules into the conical flask *A* and quickly reassemble the apparatus. Allow the reaction to proceed for 45 to 60 minutes at room temperature.

5.2.2.2 *Spectrophotometric measurements* — Disconnect the absorption tube and tilt the absorber so that the reagent solution flows back and forth between the absorber and bulb to disperse the solid contents, if any, and to mix in the solution well. Transfer the solution to a photometric cell and measure its absorbance at the wavelength of maximum absorption, 540 nm, using water as reference liquid.

NOTE — The colour of the dispersion is not very stable for long time and hence absorptiometric (nephelometric) measurement should be made within 2 hours of the development of colour. Care should also be taken to prevent the evaporation of solution as its volume is small.

In the case of fritted glass absorber raise and lower the connecting tube into the absorber several times, to allow the solution to pass through the frit back and forth effecting the dispersal of the red deposit. Let the connecting tube finally drain into the absorber.

10 µg standard shall have an absorption of the order of 0·4.

5.2.2.3 *Plotting of the calibration curve* — Calculate corrected absorbance by subtracting the reading obtained for the solution containing no standard arsenic solution from the observed reading. Plot a graph of corrected absorbance of solution against their arsenic contents.

5.2.3 The test solutions shall be prepared as prescribed in relevant individual material specifications so as to contain 1 to 10 μg of arsenic in a solution of 5·0 ± 0·5 ml volume. Transfer the solution to the conical flask, cool to room temperature if necessary and proceed as prescribed in **5.2.2**, **5.2.2.1** and **5.2.2.2**.

5.2.4 *Blank Test* — Carry out a blank test, as prescribed in **5.2.2**, **5.2.2.1** and **5.2.2.2** omitting the sample.

5.2.5 *Calculation* — Calculate the corrected absorbance by subtracting the value obtained for the blank solution from that obtained for the test solution and read from the calibration curve the corresponding mass of arsenic.

$$\text{Arsenic content, parts per million by mass} = \frac{M_1}{M_2}$$

where

M_1 = mass in μg of arsenic found, and

M_2 = mass in g of sample in the solution tested.

APPENDIX A

(*Clauses* 0.4 *and* 5.1)

PREPARATION OF TEST SOULTIONS OF ARSENIC

A-1. PREPARATION OF SOLUTION

A-1.0 The preparation of test solutions may be considered under the three possibilities described in **A-1.1** to **A-1.3**.

A-1.1 Sample Solution — A large portion of samples may be simply dissolved in water, with or without concentration, bromine treatment or addition of acid.

A-1.2 Wet Oxidation — The organic matter is destroyed and arsenic compounds not directly reducible under conditions of test are broken down. Care shall be taken that fuming of the acid does not start until all the peroxide is used up for destruction of organic compounds. Generally, 50 percent (*v/v*) hydrogen peroxide is used for destruction of organic compounds.

A-1.3 Solution of Difficult-to-Dissolve Substances

A-1.3.1 For opening up of siliceous materials; a mixture of hydrofluoric and sulphuric acid may be used but some hydrogen peroxide should be added before fuming of sulphuric acid starts.

A-1.3.2 Fusion with a mixture of sodium peroxide and sodium carbonate is useful in some cases where direct treatment with acids is not effective. If the sample is highly ferrogenous as in case of iron, ore, borax may be added in equal quantity.

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